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Article

A Comparative Investigation on the Characteristics of Nocturnal Ozone Enhancement Events and Their Effects on Ground-Level Ozone and PM_{2.5} in the Central City of the Yellow River Delta, China, in 2022 and 2023

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Abstract: In recent years, nocturnal ozone enhancement (NOE) events have become a hot research topic in the field of atmospheric environment. By using statistically-based data analysis, we made a comparative investigation about nocturnal ozone concentrations and NOE events in 2022 and 2023, and further explored the effects of NOE events on O₃ and PM_{2.5} at the night of the same day and the next day. The results showed that from 2022 to 2023 in Dongying, the annual average nocturnal ozone concentrations increased from 51 μg/m³ to 59 μg/m³, and the frequency of NOE events was higher in spring, summer and autumn, and lower in winter. NOE events not only had an obvious promoting effect on nocturnal O₃ and O_x, and the daily maximum 8 h average concentration of O₃ (MDA8-O₃) of the same day (more apparent in summer and autumn), and nocturnal PM_{2.5} and PM_{2.5}-bounded NO₃⁻ and SO₄²⁻ (more apparent in winter), but also had a distinct influence on O₃, O_x and MDA8-O₃ of the next day (more apparent in summer). The results could strengthen the understanding of the phenomena of NOE events, and provide a scientific basis for the collaborative control of PM_{2.5} and ozone in urban areas in the Yellow River Delta, China.

Keywords: nocturnal ozone(O₃); PM_{2.5}; effect; secondary pollution; the Yellow River Delta

1. Introduction

Ground-level ozone (O₃) is mainly produced by precursors such as nitrogen oxides (NO_x) and volatile organic compounds (VOCs) under light conditions [1–5]. Due to the synthetic effects of photochemical generation, dry depositions and boundary layer entrainment, the diurnal variation of ozone concentration usually presents a unimodal distribution, that is, the concentration is higher during the daytime and lower at nighttime, which has been confirmed by a large number of field observations[6–11]. However, in recent years, many studies have found that the nocturnal ozone concentrations are surging rather than falling, and the nocturnal ozone peak occurs, which has been widely observed in the United States, Europe, and China[12–19]. Studies reported that higher nocturnal ozone concentrations may have an impact on atmospheric chemical processes, human health, and vegetation growth[15,20–22]. Wang et al. [21] suggested that the increase in nocturnal ozone concentrations in China in recent years has led to an increase in the nocturnal atmospheric oxidation capacity in China. Agathokleous et al. [18,23] believed that nocturnal ozone enhancement (NOE) may adversely affect plant and animal growth. Therefore, it is necessary to carry out in-depth research on nocturnal ozone enhancement.

At present, many investigations have been performed on the characteristics and causes of NOE. He et al. [14] found that the average annual frequency of NOE events ranged from 28% to 41% in

China, the United States, and the European Union, and the frequency of NOE events in China was significantly higher than that in the United States and the European Union. Wu et al. [24] studied the NOE events and their causes in the Pearl River Delta, and found that the annual average frequency of NOE events was 53 days per year, and the average nocturnal ozone peak was $58 \mu\text{g}/\text{m}^3$. The low-level jet stream is the main meteorological process that triggers the NOE events, accounting for an average of 61%, and convective storms accounting for about 11%. In addition, sea-land breeze and mountain-valley circulations, typhoons, and stratospheric ozone intrusion also contribute to NOE events[25–29]. Few studies have speculated on the chemical effects of NOE events. Wu et al. preliminarily explored the relationship between nocturnal ozone concentration and the daily maximum 8 h average concentration of O_3 (MDA8- O_3) of the following day, and found that there was a good correlation between them[24]. He et al. [30] suggested that the NOE would lead to a persistently high value of 8 h average ozone concentration from night to the early next morning. He et al. [31] found that nocturnal $\text{PM}_{2.5}$ concentrations and odd oxygens ($\text{O}_x = \text{NO}_2 + \text{O}_3$) were significantly higher during NOE events in the Pearl River Delta region of China than during non-nocturnal ozone enhancement(NNOE) events. At present, there are few studies on the effects of NOE on secondary pollutants, and little detailed analysis has been carried out, such as the effect of NOE on secondary pollutants on the interannual and monthly scales. Most of the current studies focus on the developed regions of China, such as the North China Plain and the Pearl River Delta, and there are few studies on the Yellow River Delta.

Dongying is a central city of China's Yellow River Delta, bordered by the Bohai Sea to the east and north. In recent years, the air quality in Dongying has improved significantly, but the problem of ozone pollution is still prominent[32–34]. An et al. found that the nocturnal ozone concentration increased significantly in Dongying from 2017 to 2022, and the average nocturnal ozone concentration in the ozone pollution season in 2022 increased by $12 \mu\text{g}/\text{m}^3$ compared with 2017, which was greater than the increase during the daytime, suggesting an increase in the nocturnal atmospheric oxidation capacity in this region[35]. In addition, the NOE events were frequent in the Yellow River Delta, China, such as on the night of June 17, 2022, when there were thundershowers, the ozone concentration remained at a high level, accompanied by three increases. However, there is a lack of systematic characteristic analysis of the NOE events in this region. There is no detailed analysis of the impact of NOE events on $\text{PM}_{2.5}$ and its secondary components in Dongying City. Therefore, it is necessary to analyze the characteristics of the NOE events and their impact on ozone and $\text{PM}_{2.5}$ in Dongying City.

Based on the data of normal pollutants and $\text{PM}_{2.5}$ components concentrations in Dongying, a central city of the Yellow River Delta, China, this study analyzed the characteristics of nocturnal ozone concentration and NOE events in Dongying, and further explored the effects of NOE events on the concentrations of O_3 , O_x , $\text{PM}_{2.5}$, nitrate (NO_3^-), sulfate (SO_4^{2-}) and secondary organic carbons (SOC) at night and the next day. The results of this study are helpful to understand the characteristics of nocturnal ozone concentration and the NOE events in the Yellow River Delta, and to clarify the impact of NOE events on secondary pollutants. This study could strengthen the understanding of the phenomena of NOE events, and provide a scientific basis for the collaborative control of $\text{PM}_{2.5}$ and O_3 in urban areas in the Yellow River Delta, China.

2. Materials and Methods

2.1. Observation Period and Location

Dongying, located in the northern part of Shandong Province in China and bordered by the Bohai Sea to the east and north, is an important passage to the sea in the Yellow River Basin and a central city of the Yellow River Delta, China[36]. The hourly concentration data of normal pollutants (O_3 , SO_2 , NO_2 and $\text{PM}_{2.5}$), $\text{PM}_{2.5}$ -bounded ionic components, organic carbon (OC), and elemental carbon (EC) used in this study were obtained from the Dongying Atmospheric Observatory ("Atmospheric Observatory", Figure 1). The study duration was from January 1, 2022, to December 31, 2023. The Atmospheric Observatory is mainly surrounded by residential areas and commercial

office areas, with convenient transportation and no obvious industrial pollution sources, which can accurately reflect the air pollution situation in Dongying city (Figure 1). All observation items were continuously monitored using automatic monitoring devices, among which the SO₂, NO-NO₂-NO_x and O₃ were monitored with 43i, 42i and 49i (Thermo Fisher Scientific Inc., Waltham, MA, USA), respectively. Particulate matters were monitored online with BAM1020 (Met One Instruments Inc., Washington, DC, USA). The ion component analyzer model was S-611EG (Zhang Jia Ltd., Taiwan, China). and the OC and EC analyzer model was OCEC-100 (Focused Photonics Inc., Hangzhou, Zhejiang, China).

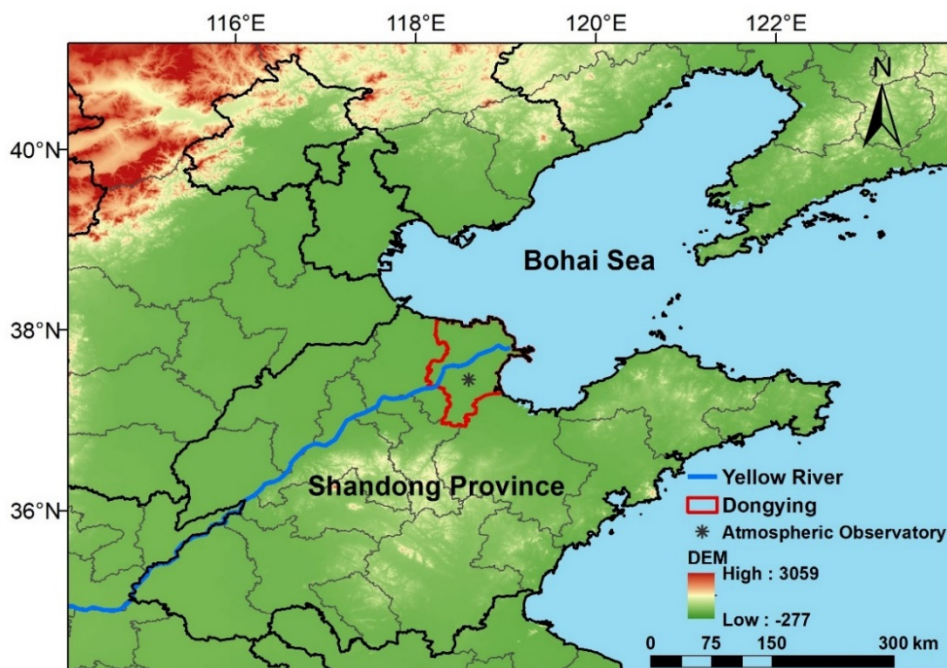


Figure 1. Geographic location of Dongying city.

2.2. Relevant Definitions

According to the characteristics of solar radiation in Dongying, the solar radiation intensity from 20:00 to 6:00 of the next day is 0, so the period from 20:00 to 6:00 of the next day is considered to be the nighttime of Dongying[14,35].

Nocturnal ozone enhancement events(NOE events): Based on the definitions of NOE events in previous studies[14,24,31], NOE events are defined as the ozone concentration increases by more than 10 $\mu\text{g}/\text{m}^3$ in two successive hours of a given night (20:00 to 06:00 of the next day), and the corresponding nocturnal maximum O₃ concentration is called the nocturnal ozone peak.

Non-nocturnal ozone enhancement events(NNOE events): nights that NOE events do not occur during the study period are defined as NNOE events.

2.3. Data Processing

2.3.1. Transformation Rate of Nitrates and Sulfates

In this study, the transformation rate of nitrates (NOR) and the transformation rate of sulfates (SOR) were used to determine the transformation status of gaseous precursors such as NO₂ and SO₂ to form secondary inorganic ions. The higher the values of NOR and SOR, the higher the degree of secondary transformation of NO₂ and SO₂ in the atmosphere. The equations are as follows:

$$NOR = N_1 / (N_1 + N_2) \quad (1)$$

$$SOR = S_1 / (S_1 + S_2) \quad (2)$$

where, N₁ and N₂ represent the concentration of NO₃⁻ and NO₂ respectively, in mol/m³; S₁ and S₂ represent the concentration of SO₄²⁻ and SO₂ respectively, in mol/m³.

2.3.2. Calculation of Secondary Organic Carbon

In this study, the OC/EC ratio method was used to calculate the mass concentration of SOC. The formula is as follows:

$$SOC = OC - EC \times (OC/EC)_{min} \quad (3)$$

where, SOC represents secondary organic carbon in $\mu\text{g}/\text{m}^3$; OC and EC represent organic carbon and elemental carbon respectively, and $(OC/EC)_{min}$ is the minimum value of OC/EC during the observation period.

3. Results and Discussion

3.1. Characteristics of Nocturnal Ozone Concentration in Dongying

3.1.1. Inter-Annual and Inter-Monthly Variations

From 2022 to 2023, the annual average nocturnal ozone concentration increased from $51 \mu\text{g}/\text{m}^3$ to $59 \mu\text{g}/\text{m}^3$ in Dongying (Figure 2). The different percentiles of nocturnal ozone hourly concentrations increased in Dongying from 2022 to 2023, ranging from 1 to $15 \mu\text{g}/\text{m}^3$ (Figure 3). The increasing range of ozone concentration from highest to lowest was the 95th percentile, 75th percentile, 50th percentile, 25th percentile, 99th percentile, and 5th percentile. It can be seen that the high and middle percentile of nocturnal ozone concentration increased most significantly in Dongying from 2022 to 2023. The increase in nocturnal ozone concentrations in Dongying is similar to the results of Li et al., who found that nocturnal ozone concentrations increased significantly in most regions of China in the summer of 2019 compared to 2015[15].

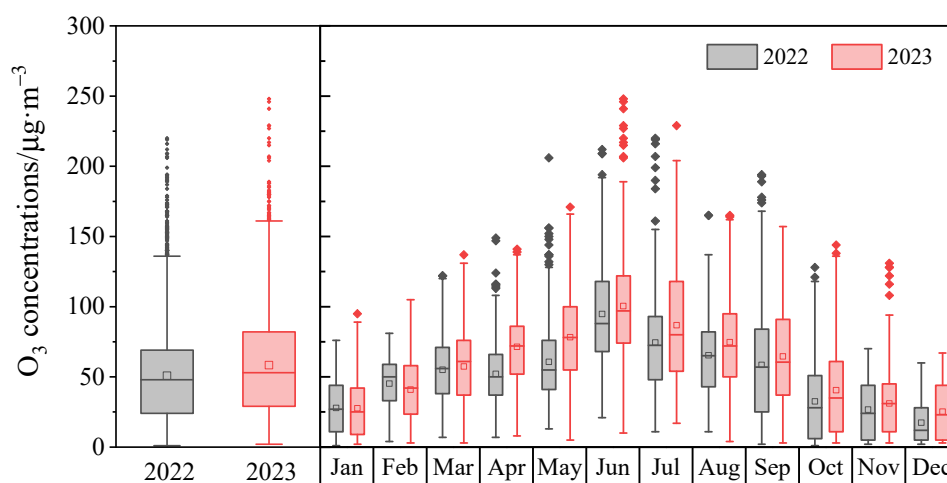


Figure 2. Inter-annual and inter-monthly changes of nocturnal ozone concentration in Dongying from 2022 to 2023.

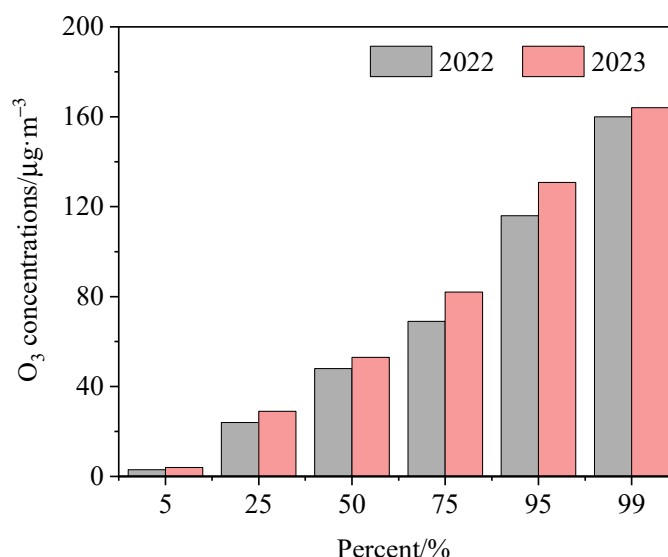


Figure 3. Characteristics of different percentiles of nocturnal ozone concentration in Dongying from 2022 to 2023.

From 2022 to 2023, the monthly variation of nocturnal ozone concentration in Dongying showed an unimodal distribution, with the peak occurring in June (Figure 2). The nocturnal ozone concentration was low from January to February and from October to December, with a monthly average value of 17-45 $\mu\text{g}/\text{m}^3$. From March to September, the nocturnal ozone concentration was high, with a monthly average value of 52-100 $\mu\text{g}/\text{m}^3$. This was consistent with the monthly variation of MDA8-O₃ in Dongying[35]. The nocturnal ozone concentration was higher in the ozone pollution season and lower in the non-ozone pollution season, indicating that the nocturnal ozone concentration was closely related to the daytime ozone pollution. The nocturnal ozone concentrations from February to December 2023 were higher than those in 2022, and the most significant increases were in April to May and July, with an increase of 12-19 $\mu\text{g}/\text{m}^3$ (Figure 2). The increase of nocturnal ozone concentration in Dongying in the past two years suggests that attention should be paid to the NOE in the Yellow River Delta, which may alter the nighttime atmospheric oxidation capacity and further affect atmospheric chemical reactions.

3.1.2. Diurnal Variation

From 2022 to 2023, the diurnal variation of nocturnal ozone concentration showed a decreasing trend or weak unimodal distribution in Dongying (Figure 4). The diurnal variation of nocturnal ozone concentration during the ozone pollution season (April to September) showed a significant decreasing trend, while the diurnal variation from January to February and November to December showed a weak unimodal distribution. Most of the nocturnal ozone concentrations increased slightly from 1:00 to 6:00, with an average increase of 1 to 2 $\mu\text{g}/\text{m}^3$. Compared with 2022, the nocturnal ozone concentration in Dongying increased significantly from April to November 2023, and the increase was the most apparent in July, with an average increase of 25 $\mu\text{g}/\text{m}^3$ from 20:00 to 21:00. This was followed by 21:00 to 1:00 of the next day in April (an average increase of 21 $\mu\text{g}/\text{m}^3$), 20:00-0:00 in May (an average increase of 20 $\mu\text{g}/\text{m}^3$), 2:00-6:00 in December (an average increase of 20 $\mu\text{g}/\text{m}^3$) and 20:00-22:00 in October (an average increase of 19 $\mu\text{g}/\text{m}^3$). This may be due to the higher daytime ozone concentration in Dongying in 2023. The 90th percentile of MDA8-O₃ was 221 $\mu\text{g}/\text{m}^3$ in Dongying in July 2023, with an increase of 30 $\mu\text{g}/\text{m}^3$ compared with 2022. Higher ozone concentrations during the day in July 2023 led to higher ozone concentrations at night.

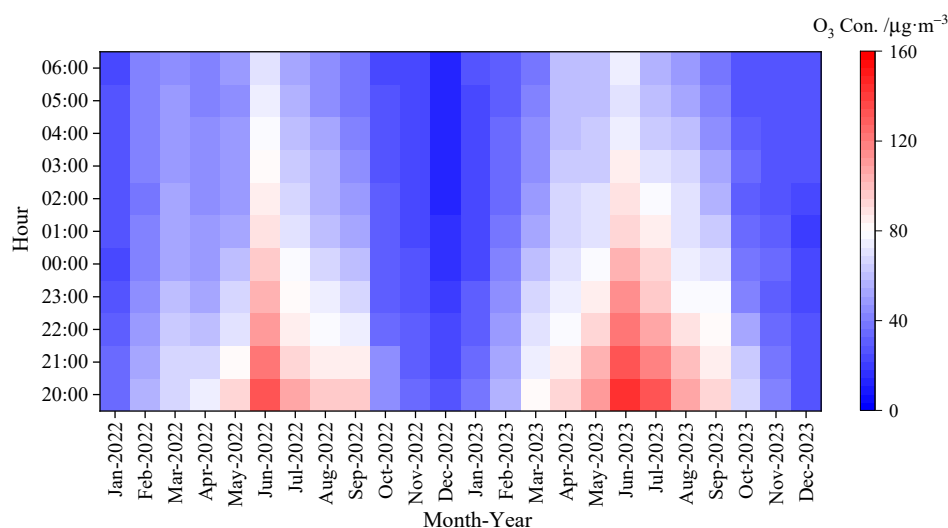


Figure 4. Diurnal variation of nocturnal ozone concentration in Dongying from 2022 to 2023.

3.2. Characteristics of Nocturnal Ozone Enhancement Events in Dongying

3.2.1. Frequency Characteristics

NOE events in Dongying from January 1, 2022, to December 31, 2023 were selected. The results showed that the annual average frequency of NOE events was 44% and 43% in Dongying in 2022 and 2023, respectively. This is comparable to the results of He et al.'s research on the frequency of NOE events in China[14]. In terms of the monthly frequency of NOE events, the frequency of NOE events in Dongying was the highest in March (56%), followed by September (55%), October (52%), June (50%), May (48%), and August (48%). The lowest frequency of NOE events (27%) occurred in July (Figure 5). Overall, the frequency of NOE events in Dongying was higher in spring, summer and autumn, and lower in winter from 2022 to 2023. The frequency was 29%, 46%, 58%, 43%, 55%, 47%, 32%, 39%, 63%, 42%, 47%, and 23% from January to December 2022, and 32%, 36%, 55%, 47%, 42%, 53%, 23%, 58%, 47%, 61%, 33%, and 32% from January to December 2023, respectively. Among them, the frequency of NOE events from February to March, May, July, September, and November 2023 decreased compared with 2022, while the frequency in January, April, June, August, and December increased compared with 2022, and the largest increase was in August. This might be related to changes of pollutant emissions and meteorological conditions in Dongying.

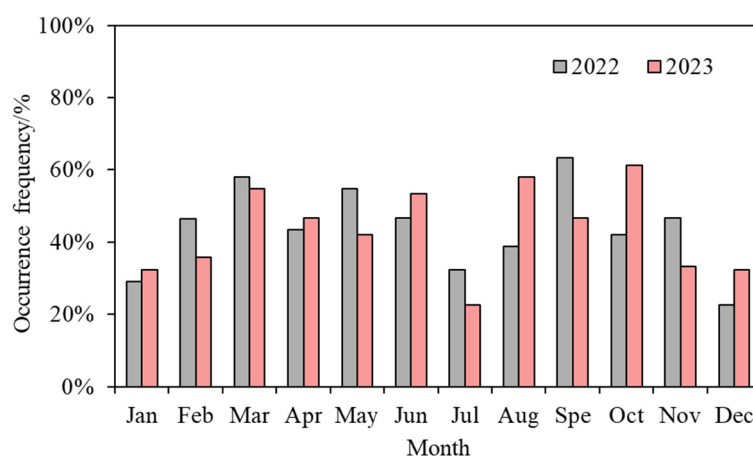


Figure 5. The occurrence frequency of NOE events in Dongying during different months from 2022 to 2023.

The occurrence frequency of NOE events from 21:00 to 6:00 in Dongying in 2022 was 10%, 9%, 10%, 7%, 9%, 14%, 14%, 11%, 8%, and 8% (Figure 6); and they were 10%, 7%, 7%, 8%, 8%, 14%, 11%, 12%, 8%, and 15% in 2023 (Figure 6). Among them, the frequency of NOE events from 22:00 to 23:00, 1:00, and 3:00 in 2023 decreased compared with 2022, while the frequency at 0:00, 4:00, and 6:00 increased compared with 2022. Overall, the frequency of NOE events was the highest at 2:00 in Dongying, with a total of 66 events during the two years, followed by 3:00, 4:00 and 6:00. In 2022 and 2023, the diurnal variation characteristics of the frequency of NOE events in Dongying were generally comparable, with a higher frequency from 2:00 to 4:00 and a lower frequency from 21:00 to 1:00 of the next day. This might be because the strong NO_x titration after sunset made NOE events less likely to occur in the early nocturnal period, while the ozone concentration decreasing in the late nocturnal due to the diffusion, transport, and deposition of ozone was not conducive to the formation of NOE events [14,24,37].

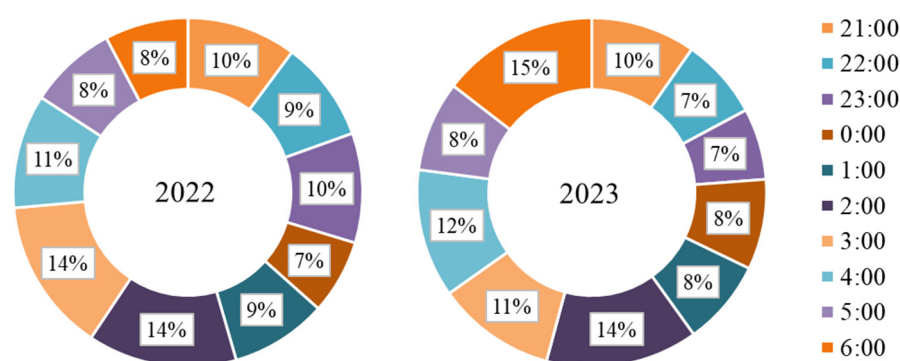


Figure 6. The occurrence frequency of NOE events in Dongying at different times from 2022 to 2023.

3.2.2. Characteristics of Nocturnal Ozone Peak and Ozone Increase Magnitude

The distribution of nocturnal ozone peaks in Dongying from 2022 to 2023 is shown in Figure 7. Most nocturnal ozone peaks were 40-60 $\mu\text{g}/\text{m}^3$ (125), followed by 20-40 $\mu\text{g}/\text{m}^3$ (99), 60-80 $\mu\text{g}/\text{m}^3$ (91), and 80-100 $\mu\text{g}/\text{m}^3$ (67). During the study period, the nocturnal ozone peak was above 160 $\mu\text{g}/\text{m}^3$ for 6 times, and the maximum nocturnal ozone peak was 210 $\mu\text{g}/\text{m}^3$. This is comparable to the maximum of nocturnal ozone peaks in Jinan, China, Shenzhen, China, and Malaysia [38-40]. It could be seen that Dongying, a central city of the Yellow River Delta, had extremely high nocturnal ozone peaks when NOE events occurred, which might have adverse effects on human health. From 2022 to 2023, most ozone increase magnitude ($\Delta\text{O}_3/\Delta t$) in NOE events in Dongying was 10-20 $\mu\text{g}/\text{m}^3$, followed by 20-30 $\mu\text{g}/\text{m}^3$, 30-40 $\mu\text{g}/\text{m}^3$, and 40-50 $\mu\text{g}/\text{m}^3$, and the maximum increase magnitude of nocturnal ozone concentration was 95 $\mu\text{g}/\text{m}^3$. This is consistent with the results of He et al. [14], which showed that the majority of nocturnal ozone increases magnitude in China ranged from 10 to 20 $\mu\text{g}/\text{m}^3$.

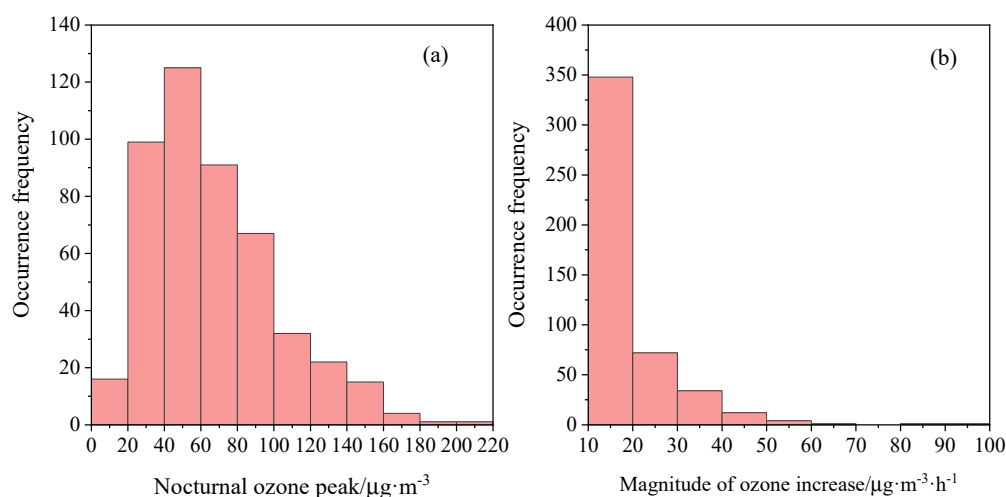


Figure 7. Distribution characteristics of (a) nocturnal ozone peak and (b) magnitude of ozone increase in Dongying from 2022 to 2023.

From 2022 to 2023, the nocturnal ozone peak in Dongying gradually decreased from 21:00 to 6:00 of the next day (Figure 8). During the study period, the nocturnal ozone peak was higher from 21:00 to 23:00, with an average value of $81 \mu\text{g}/\text{m}^3$. From 0:00 to 6:00, the nocturnal ozone peak changed slightly, and the average nocturnal ozone peak was $60 \mu\text{g}/\text{m}^3$. This is consistent with the results of Wu et al.'s research in the Pearl River Delta, which showed a gradual decreasing trend of nocturnal ozone peak from 21:00 to 6:00 of the next day[24].

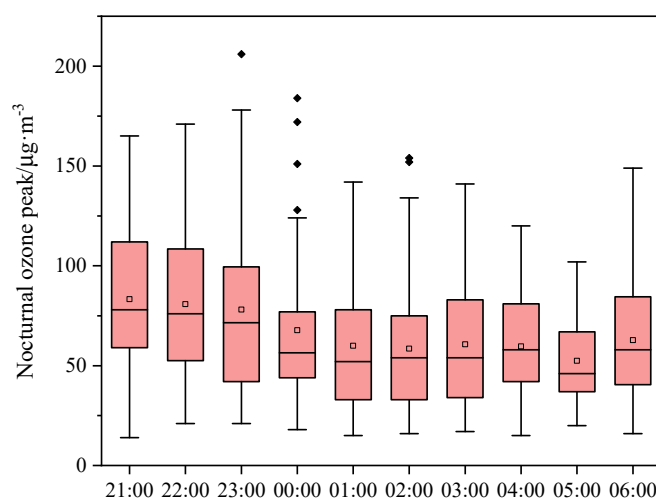


Figure 8. Distribution characteristics of nocturnal ozone peak at different times in Dongying from 2022 to 2023.

3.3. Effects of Nocturnal Ozone Enhancement Events on Ozone and $\text{PM}_{2.5}$ Concentrations in Dongying

3.3.1. Effects on Ozone and Atmospheric Oxidation at Night and the Next Day

The effects of NOE events on nocturnal ozone concentrations are as follows. In 2022 and 2023, the average nocturnal ozone concentrations during NOE events in Dongying were $4 \mu\text{g}/\text{m}^3$ and $2 \mu\text{g}/\text{m}^3$ higher than those during NNOE events, respectively. The average nocturnal ozone concentrations in NOE events in January and June to October were higher than those in NNOE events. The differences in the average nocturnal ozone concentrations were higher in January and October, with a difference of $8 \mu\text{g}/\text{m}^3$ and $6 \mu\text{g}/\text{m}^3$, respectively.

The effects of NOE events on nocturnal O_x concentrations are as follows. In 2022 and 2023, the average nocturnal O_x concentrations during NOE events in Dongying were $6 \mu\text{g}/\text{m}^3$ and $5 \mu\text{g}/\text{m}^3$

higher than those during NNOE events, respectively. The average nocturnal O_x concentrations in NOE events from January to February and June to December were distinctly higher than those in NNOE events. The differences in the average nocturnal O_x concentrations were higher in January and June, both with a difference of $8 \mu\text{g}/\text{m}^3$.

The effects of NOE events on MDA8- O_3 of the same day are as follows. In 2022 and 2023, the average MDA8- O_3 concentrations on the day of NOE events in Dongying were $11 \mu\text{g}/\text{m}^3$ and $6 \mu\text{g}/\text{m}^3$ higher than those during NNOE events, respectively. The average MDA8- O_3 concentrations in the day of NOE events in January, April, June, August, October and November were clearly higher than those in NNOE events. The differences were higher in January ($11 \mu\text{g}/\text{m}^3$) and August ($17 \mu\text{g}/\text{m}^3$).

Therefore, NOE events in Dongying from 2022 to 2023 had an obvious promoting effect on nocturnal O_3 , O_x and MDA8- O_3 of the same day, which increased by $3 \mu\text{g}/\text{m}^3$, $6 \mu\text{g}/\text{m}^3$ and $8 \mu\text{g}/\text{m}^3$, respectively, and increased distinctly in summer and autumn.

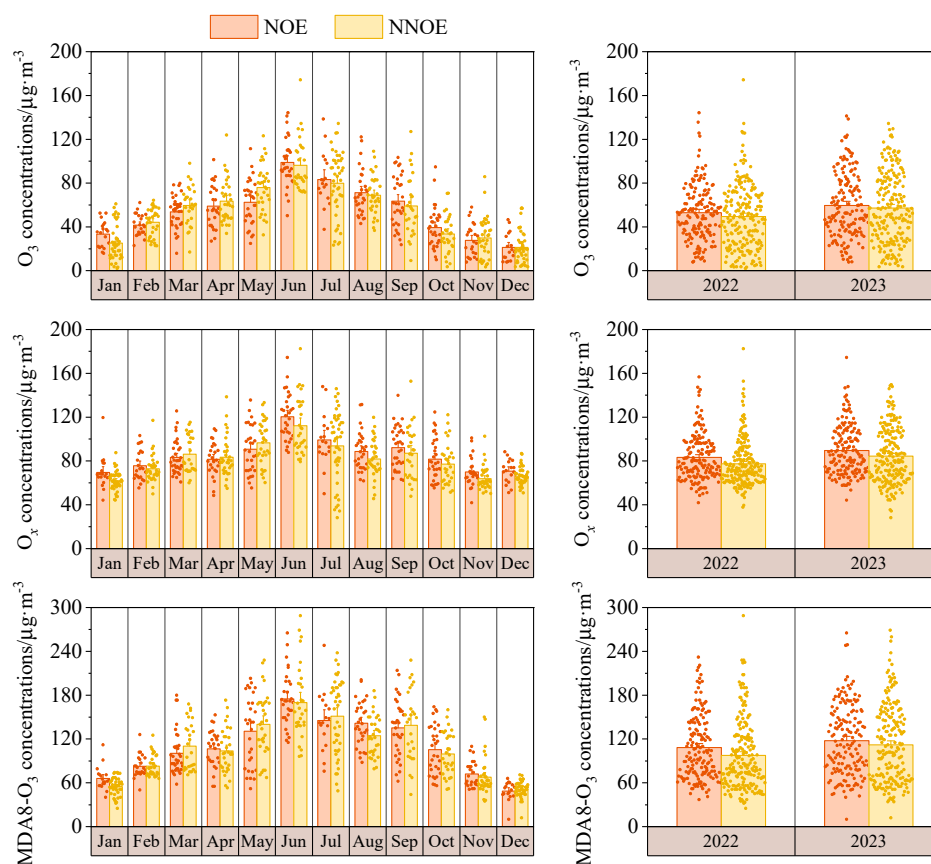


Figure 9. Difference in nocturnal O_3 , O_x and MDA8- O_3 of the same day in NOE events and NNOE events in Dongying from 2022 to 2023.

The effects of NOE events on ozone concentrations of the next day are as follows. In 2022 and 2023, the average ozone concentrations of the next day of NOE events in Dongying were $10 \mu\text{g}/\text{m}^3$ and $9 \mu\text{g}/\text{m}^3$ higher than those during NNOE events, respectively. The average ozone concentrations of the next day of NOE events were distinctly higher than those in NNOE events in every month except February and May. The differences were higher in June and July, both with a difference of $13 \mu\text{g}/\text{m}^3$.

The effects of NOE events on O_x concentrations of the next day are as follows. In 2022 and 2023, the average O_x concentrations of the next day of NOE events in Dongying were $8 \mu\text{g}/\text{m}^3$ and $9 \mu\text{g}/\text{m}^3$ higher than those during NNOE events, respectively. The average O_x concentrations on the next day of NOE events were apparently higher than those in NNOE events in every month except February and May. The differences were higher in June, July and August, with a difference of $14 \mu\text{g}/\text{m}^3$, $15 \mu\text{g}/\text{m}^3$ and $10 \mu\text{g}/\text{m}^3$, respectively.

The effects of NOE events on MDA8-O₃ of the next day are as follows. In 2022 and 2023, the average MDA8-O₃ concentrations of the next day of NOE events in Dongying were 12 $\mu\text{g}/\text{m}^3$ and 14 $\mu\text{g}/\text{m}^3$ higher than those during NNOE events, respectively. The average MDA8-O₃ concentrations of the next day of NOE events were higher than those in NNOE events in every month except March and May. The differences were higher from June to August, with a difference of 15 $\mu\text{g}/\text{m}^3$, 17 $\mu\text{g}/\text{m}^3$ and 13 $\mu\text{g}/\text{m}^3$, respectively.

Overall, NOE events in Dongying from 2022 to 2023 also had a clearly promoting effect on the O₃, O_x and MDA8-O₃ of the next day, which increased by 9 $\mu\text{g}/\text{m}^3$, 8 $\mu\text{g}/\text{m}^3$ and 13 $\mu\text{g}/\text{m}^3$, respectively, and increased significantly in summer.

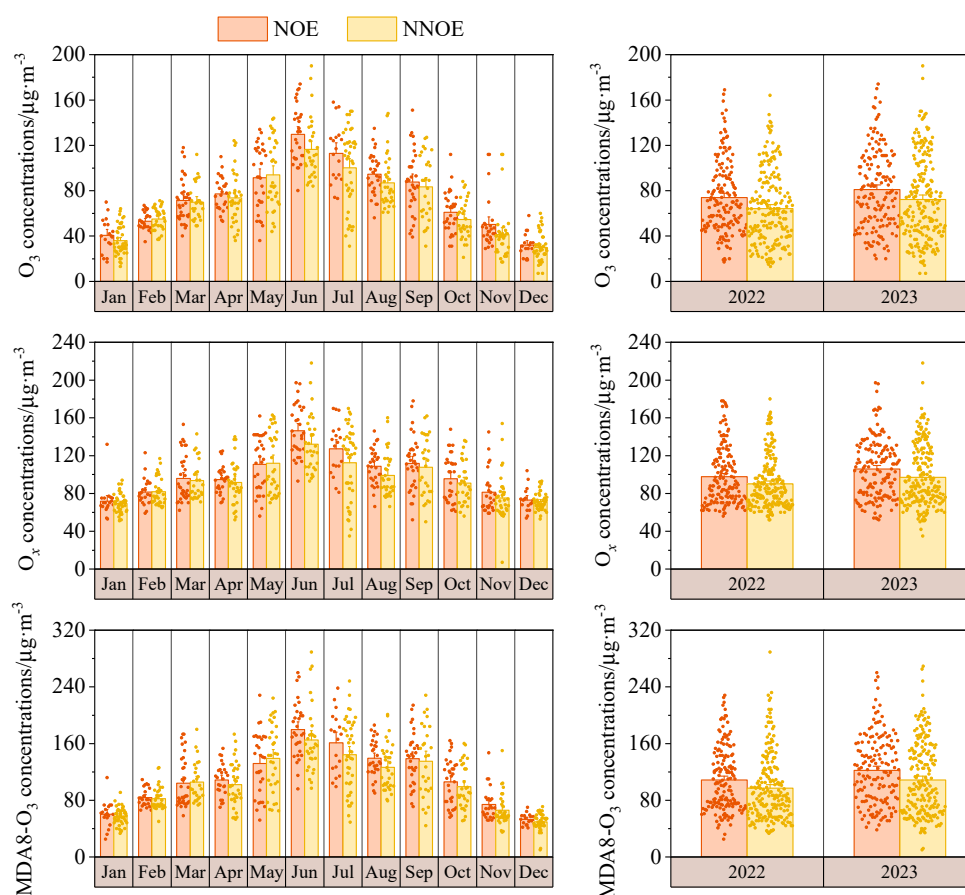


Figure 10. Difference in O₃, O_x and MDA8-O₃ of the next day in NOE events and NNOE events in Dongying from 2022 to 2023.

3.3.2. Effects on PM_{2.5} Concentration and Secondary Components at Night and the Next Day

From 2022 to 2023, there was a significant correlation between the nocturnal O_x, PM_{2.5}, PM_{2.5}-bounded NO₃⁻, SO₄²⁻ and SOC in Dongying (Figure 11), so the increase of the nocturnal atmospheric oxidation capacity in Dongying had a certain impact on PM_{2.5} concentration and its secondary components. According to the analysis in Section 3.3.1, NOE events can increase the concentration of O_x and increase the oxidation capacity of the atmosphere. Therefore, NOE events may have a certain impact on PM_{2.5} concentration and its secondary components. Hence, the effects of NOE events on the concentrations of PM_{2.5}, PM_{2.5}-bounded NO₃⁻, SO₄²⁻ and SOC in Dongying from 2022 to 2023 were further analyzed in this study.

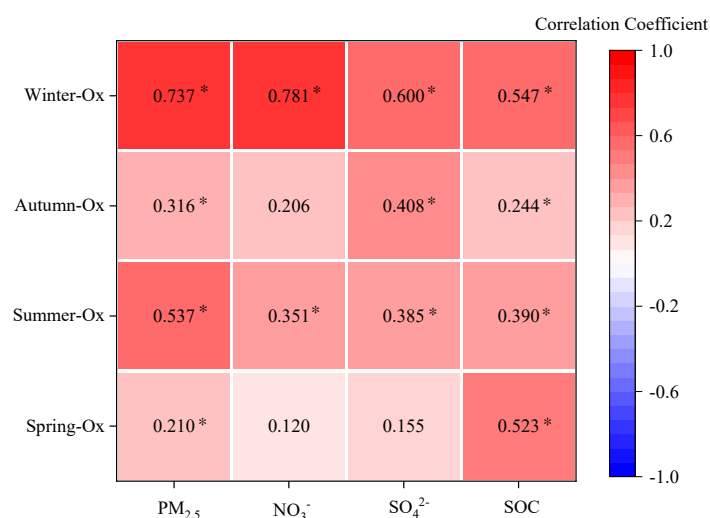


Figure 11. Correlation between O_x concentration and PM_{2.5} and PM_{2.5}-bounded components in different seasons of NOE events in Dongying from 2022 to 2023.

The effects of NOE events on nocturnal PM_{2.5} concentrations are as follows. In 2022 and 2023, the average nocturnal PM_{2.5} concentrations during NOE events in Dongying were 5 µg/m³ and 4 µg/m³ higher than those during NNOE events, respectively. The average nocturnal PM_{2.5} concentrations in NOE events were apparently higher than those in NNOE events in all months except April and September. The differences were higher in November and December, with a difference of 14 µg/m³ and 32 µg/m³, respectively.

The effects of NOE events on nocturnal NO₃⁻ concentrations are as follows. In 2022 and 2023, the average nocturnal NO₃⁻ concentrations during NOE events in Dongying were 3 µg/m³ and 2 µg/m³ higher than those during NNOE events, respectively. The average nocturnal NO₃⁻ concentrations in NOE events from January to March, November and December were higher than those in NNOE events. The differences were higher in November and December, with a difference of 7 µg/m³ and 15 µg/m³, respectively.

The effects of NOE events on nocturnal SO₄²⁻ concentrations are as follows. The nocturnal SO₄²⁻ concentrations during NOE events in Dongying in 2022 and 2023 were comparable to those during NNOE events. The nocturnal SO₄²⁻ concentrations during NOE events in January, February, November and December were 3 µg/m³, 1 µg/m³, 1 µg/m³ and 3 µg/m³ higher than those during NNOE events, respectively.

The effects of NOE events on nocturnal SOC concentrations are as follows. In 2022 and 2023, the average nocturnal SOC concentration during NOE events in Dongying was comparable to those during NNOE events, and sometimes even slightly lower than those during NNOE events. This might be due to the low accuracy of the current SOC estimation method and the complexity of the impact of nocturnal atmospheric oxidation on SOC, which could not be simply reflected by the average concentration of SOC. Further detailed research on the impact of NOE events on secondary organic components in PM_{2.5} is needed in the future.

In conclusion, NOE events had an obvious promoting effect on the nocturnal PM_{2.5}, PM_{2.5}-bounded NO₃⁻ and SO₄²⁻ in Dongying from 2022 to 2023, and the impact was most distinct in winter. NOE events had no obvious effect on the average nocturnal SOC concentration.

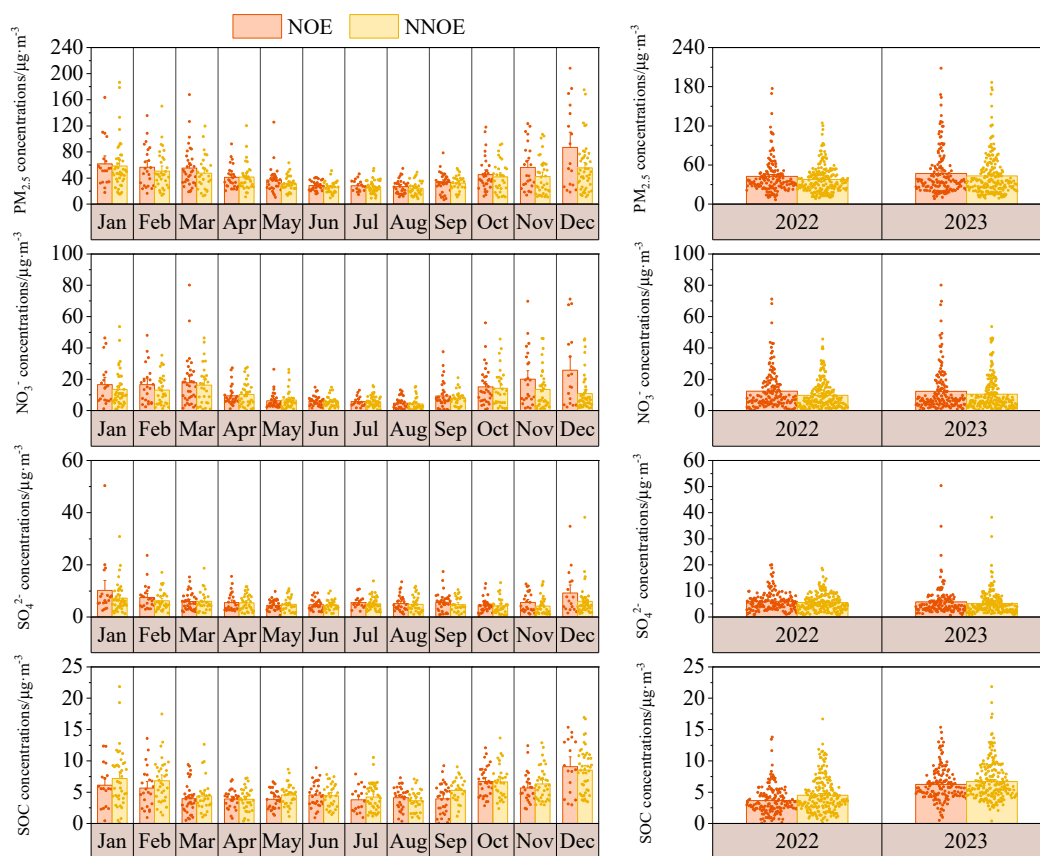


Figure 12. Difference of nocturnal $PM_{2.5}$, $PM_{2.5}$ -bounded NO_3^- , SO_4^{2-} and SOC in NOE events and NNOE events in Dongying from 2022 to 2023.

NOE events had obvious effects on nocturnal $PM_{2.5}$, $PM_{2.5}$ -bounded NO_3^- and SO_4^{2-} , therefore the differences between nocturnal NOR and SOR during NOE events and NNOE events were further analyzed in this study (Figure 13).

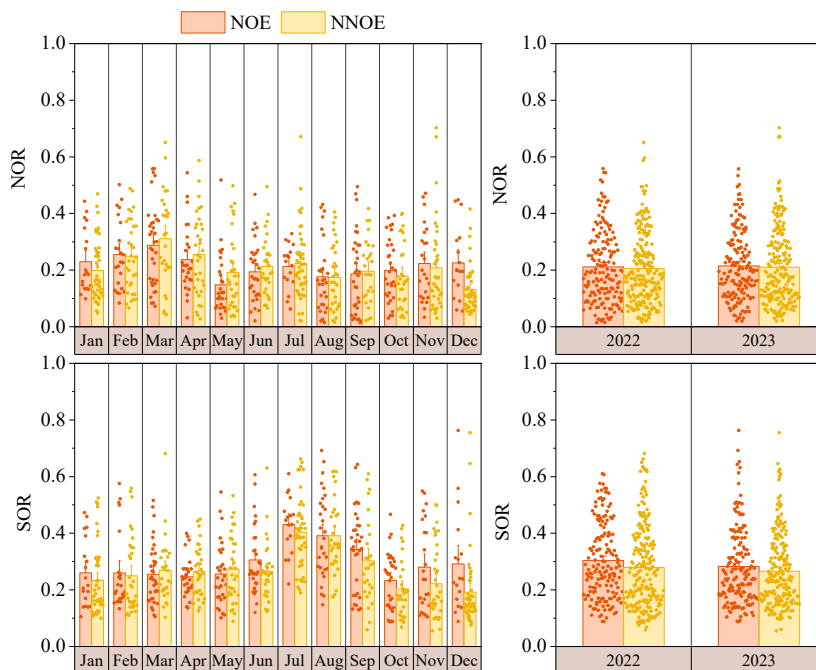


Figure 13. Difference of nocturnal NOR and SOR in NOE events and NNOE events in Dongying from 2022 to 2023.

The effects of NOE events on nocturnal NOR are as follows. The nocturnal NOR during NOE events in 2022 and 2023 were 0.006 and 0.005 higher than those during NNOE events in Dongying, respectively. The nocturnal NOR during NOE events in January, February, October to December were 0.03, 0.006, 0.02, 0.01 and 0.09 higher than those during NNOE events, respectively. This was consistent with the effect of NOE events on NO_3^- concentrations. It can be seen that NOE events may affect the concentration of NO_3^- by affecting the oxidation of nocturnal NO_2 .

The effects of NOE events on nocturnal SOR are as follows. The nocturnal SOR during NOE events in 2022 and 2023 were 0.02 higher than those during NNOE events in Dongying. The nocturnal SOR during NOE events in January, February, June, July, September, October, November and December were 0.03, 0.01, 0.04, 0.02, 0.04, 0.03, 0.06 and 0.10 higher than those during NNOE events, respectively. This was consistent with the effect of NOE events on SO_4^{2-} concentrations. It can be seen that NOE events may affect the concentration of SO_4^{2-} by affecting the oxidation of nocturnal SO_2 .

The effects of NOE events on $\text{PM}_{2.5}$ concentrations of the next day are as follows. In 2022 and 2023, the average $\text{PM}_{2.5}$ concentration on the next day of NOE events in Dongying was generally comparable to those during NNOE events. The average $\text{PM}_{2.5}$ concentration of the next day of NOE events was slightly higher than those of NNOE events in May, June, July, August, October and December, with a difference of about $3 \mu\text{g}/\text{m}^3$. Therefore, NOE events have no obvious effect on the average $\text{PM}_{2.5}$ concentration of the next day.

The effects of NOE events on NO_3^- concentrations of the next day are as follows. In 2022 and 2023, the average NO_3^- concentration on the next day of NOE events in Dongying was generally comparable to those during NNOE events. The average concentration of NO_3^- on the next day of the NOE events in December was $6 \mu\text{g}/\text{m}^3$ higher than that during the NNOE event, and there was no significant difference in other months. Therefore, the NOE event had an obvious effect on the average concentration of NO_3^- on the next day in December, but did not affect other months.

The effects of NOE events on SO_4^{2-} and SOC concentrations of the next day are as follows. The average concentrations of SO_4^{2-} and SOC on the next day of NOE events in Dongying in 2022 and 2023 were generally comparable to those during NNOE events, and they were also similar in different months. Therefore, NOE events had little effect on the average concentrations of SO_4^{2-} and SOC of the next day.

In summary, the NOE events had no obvious effect on the $\text{PM}_{2.5}$, $\text{PM}_{2.5}$ -bounded NO_3^- , SO_4^{2-} and SOC concentrations of the next day in Dongying from 2022 to 2023. The reason might be that NOE had an apparent effect on the nocturnal concentrations of $\text{PM}_{2.5}$, $\text{PM}_{2.5}$ -bounded NO_3^- and SO_4^{2-} , and the concentrations of chemical substances generated at night decreased with chemical reaction, deposition and transport, so the impact of NOE events on secondary pollutants of the next day was not as obvious as the effect on secondary pollutants at night.

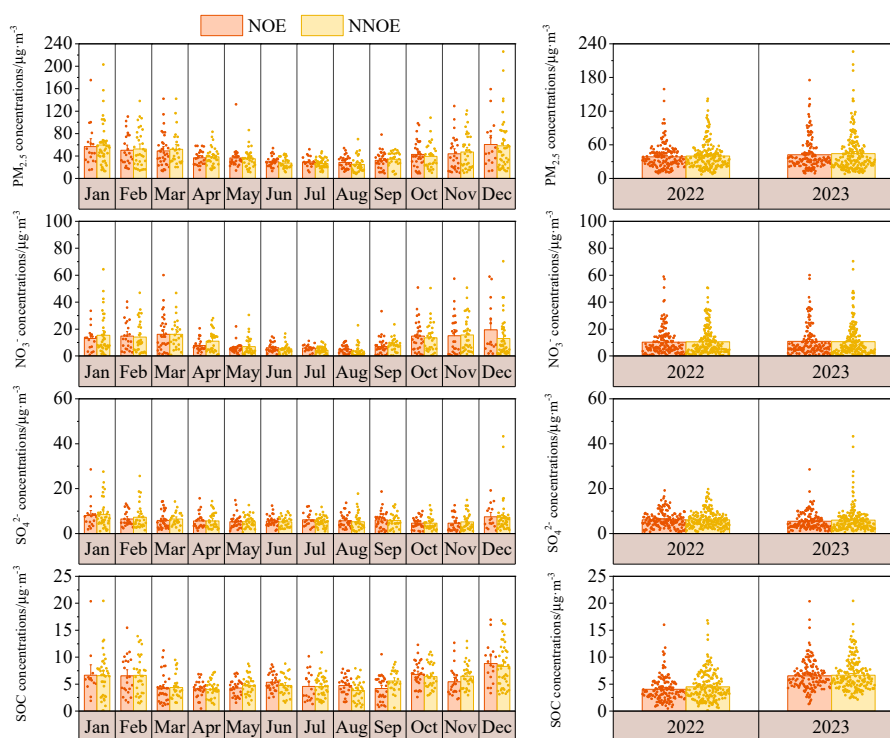


Figure 14. Difference of $PM_{2.5}$, $PM_{2.5}$ -bounded NO_3^- , SO_4^{2-} and SOC concentration of the next day in NOE events and NNOE events in Dongying from 2022 to 2023.

4. Conclusion

(1) From 2022 to 2023, the annual average nocturnal ozone concentration increased from $51 \mu\text{g}/\text{m}^3$ to $59 \mu\text{g}/\text{m}^3$ in Dongying. The different percentile values of nocturnal ozone concentration increased in Dongying in the past two years, and the high and middle percentiles increased most obviously. The nocturnal ozone concentration was higher in the ozone pollution seasons and lower in the non-ozone pollution seasons. Compared with 2022, the nocturnal ozone concentration increased most significantly in spring and summer in 2023.

(2) From 2022 to 2023, the annual average frequency of NOE events in Dongying was 44% and 43%, respectively, which was higher in spring, summer and autumn, and lower in winter. The diurnal variation characteristics of the frequency of NOE events were generally similar in 2022 and 2023, with a higher frequency from 2:00 to 4:00 and a lower frequency from 21:00 to 1:00 the next day.

(3) NOE events had an obvious promoting effect on nocturnal O_3 , O_x and $MDA8-O_3$ of the same day in Dongying from 2022 to 2023, and the increase was more apparent in summer and autumn. NOE events also had a distinct effect on the O_3 , O_x and $MDA8-O_3$ of the next day, and it was the most obvious in summer. From the perspective of government control, it is necessary to judge the ozone pollution status of the next day concerning the characteristics of nocturnal ozone changes. Furthermore, NOE events had an obvious effect on nocturnal concentrations of $PM_{2.5}$ and $PM_{2.5}$ -bounded NO_3^- and SO_4^{2-} , and the impact was most apparent in winter. NOE events had no obvious effect on concentrations of $PM_{2.5}$, $PM_{2.5}$ -bounded NO_3^- , SO_4^{2-} and SOC of the next day.

(4) NOE events have distinct effects on the concentrations of O_3 , O_x , $MDA8-O_3$, $PM_{2.5}$, and $PM_{2.5}$ -bounded NO_3^- and SO_4^{2-} . This suggests that NOE events can improve atmospheric oxidation capacity and promote the formation of $PM_{2.5}$ and its secondary components, which have a certain impact on air quality. Therefore, we need to pay more attention to the occurrence of NOE events and the challenges brought by NOE to the coordinated control of $PM_{2.5}$ and ozone, and use more refined methods to research the effect of NOE on atmospheric oxidation capacity and $PM_{2.5}$ and its secondary components in the future. In addition, with the increasing of human nocturnal activities, it is also necessary to study the impact of NOE on human health and biological growth.

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Conflicts of Interest: Author Luyao Tan was employed by the company Ltd. of Shandong Environmental Protection Industry Corp. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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